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STEREOCHEMISTRY IN ALKYLATIONS OF DIANIONS OF β-HYDROXYSULFOXIDES AND β-HYDROXYSULFONES

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Summary: Alkylations of dianions of β-hydroxysulfoxides and β-hydroxysulfones have been found to be affected by chelation of a Li cation with a sulfinyl group and by coordination of the cation with tetrahydrofuran rather than a sulfonyl group, respectively.

Dianions of the compounds containing an electron-withdrawing group and a hydroxyl group at the 1- and 2-positions are widely applicable to organic synthesis. Dianions of β-hydroxysulfones are reactive towards a variety of electrophiles,1) and have been employed for preparation of some lactones.1-3) However, the stereochemical problem in alkylations of these dianions have not been elucidated. Here we wish to report the stereochemistry in the alkylations of dianions of $(S^*_S,2S^*)$- and $(R^*_S,2S^*)$-1-phenylsulfinyl-2-alkanols (1 and 2), and 1-phenylsulfonyl-2-alkanols (3).

The sulfoxides 1 and 2 were prepared by stereoselective reduction of the corresponding ketones with diisobutylaluminum hydride in the presence or absence of $ZnCl_2$,4) and purified by column chromatography on silica gel.

Treatment of the dianions generated from 1-3 and butyllithium (2.2 equiv.) with alkyl iodide in tetrahydrofuran (THF) at -78 °C yielded a diastereoisomeric mixture of *syn*- and *anti*-products [(4A-6A) and (4B-6B)].5) The configurations of 6A and 6B were determined by J_{H_α,H_β} values in their ^{1}H NMR spectra,6) and those of 4 and 5 were determined by the similar NMR observation after converting 4 and 5 to the corresponding sulfones 6 with *m*-chloroperbenzoic acid. Further treatment of one isomer of 4-6 with butyllithium at -78 °C resulted in no interconversion to the other isomer. These results are shown in Table 1.

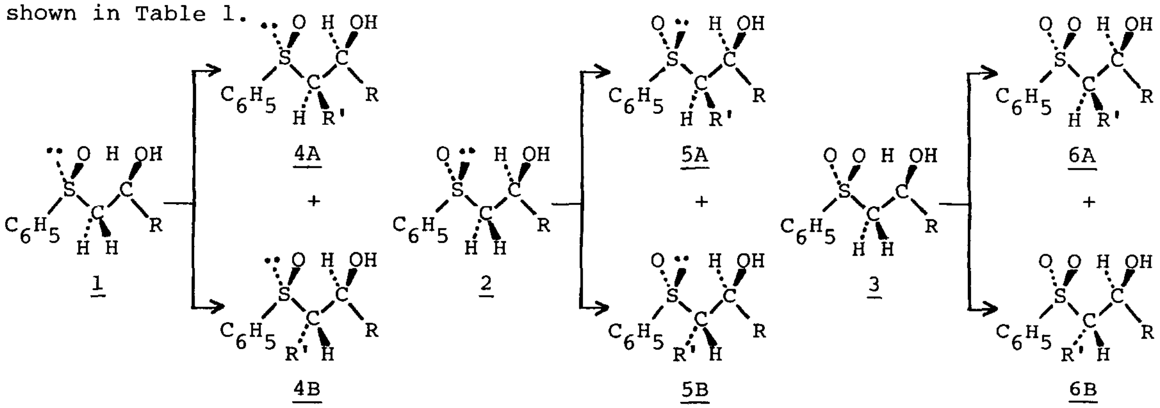
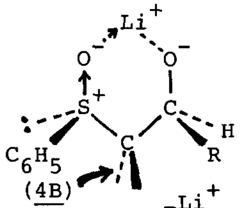


Table 1. Alkylations of dianions of 1-3

	R	R'	4A/4B[a] (Yield/%)[b]	5A/5B[a] (Yield/%)[b]	6A/6B[a] (Yield/%)[b]
a	CH_3	CH_3	11/89 (86)	22/78 (86)	51/49 (98)
b	$(CH_3)_2CHCH_2$	CH_3	4/96 (96)	28/72 (96)	78/22 (72)
c	n-C_9H_{19}	CH_3	5/95 (70)	19/81 (72)	78/22 (72)
d	$C_6H_5CH_2$	CH_3	3/97 (84)	5/95 (58)	85/15 (62)
e	n-C_9H_{19}	n-C_8H_{17}	1/99 (59)	2/98 (42)	83/17 (45)

[a] Determined HPLC. [b] Isolated yield.

1



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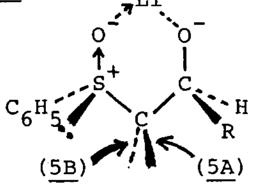

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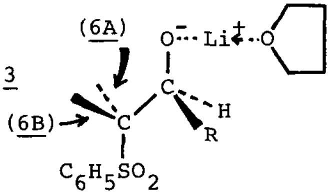

Interestingly, alkylations of the dianions of 1 occurred stereoselectively, the 5A/5B ratio was quite different from the corresponding 6A/6B ratio (*e.g.*, 5Ad/5Bd = 5/95, whereas 6Ad/6Bd = 85/15), and the stereoselectivity in formation of 5 and 6 increased with increasing bulkiness of R and R'. When alkylation of 3c (R = n-C_9H_{19}) with methyl iodide was carried out in THF containing *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 2.2 equiv.) or hexamethylphosphorus triamide (HMPA, 2.2 equiv.) at -78 °C, the 6Ac/6Bc ratio changed respectively to 72/28 or 56/44, but neither TMEDA nor HMPA affected the stereochemistry of the methylations of 1c and 2c.

These findings may be explained as follows. An alkoxide group ($-O^-Li^+$) in the dianion of 3 coordinates with THF or TMEDA rather than a sulfonyl group. On the other hand, chelation of Li cation with an alkoxide group and a polar sulfinyl group plays an important role in both dianions of 1 and 2.

Although chelation between a carbonyl group and a sulfinyl group sometimes requires Zn cation,7) Li cation is effective in chelation of an alkoxide anion and a sulfinyl group. The present results provide the significant information regarding to coordination of a metal cation with THF or TMEDA.8-12)

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References and Notes

1) K. Tanaka, K. Ootake, K. Imai, N. Tanaka, and A. Kaji, *Chem. Lett.*, 1983, 633. 2) G. Solladié, C. Fréchou, G. Demailly, and C. Greck, *J. Org. Chem.*, 51, 1912 (1986). 3) A. P. Kozikowski, B. B. Megrage, C. S. Li, and L. Felder, *Tetrahedron Lett.*, 27, 4817 (1986). 4) H. Kosugi, H. Konta, and H. Uda, *J. Chem. Soc., Chem. Commun.*, 1985, 211. 5) After addition of butyllithium it is essential to warm the resulting solution to -20 °C and again to cool to -78 °C. Alkylation of dianions of 1 and 2 has not been carried out successfully without this procedure.2) 6) For example, 6Aa; $J_{H\alpha,H\beta}$ = 1.22 Hz and 6Ba; $J_{H\alpha,H\beta}$ = 7.02 Hz. 7) Ref. 4) and references cited therein. 8) G. Boche, M. Marsch, K. Harms, and G. M. Sheldrick, *Angew. Chem. Int. Ed. Engl.*, 24, 573 (1985). 9) G. Boche, M. Marsch, and K. Harms, *Angew. Chem. Int. Ed. Engl.*, 25, 373 (1986). 10) G. W. Klumpp, *Recl. Trav. Chim. Pays-Bas.*, 105, 1 (1986). 11) P. Strazewski and C. Tamm., *Helv. Chim. Acta*, 69, 1041 (1986). 12) R. A. Wanat, D. B. Collum, G. V. Duyne, J. Clardy, and R. T. Depue, *J. Am. Chem. Soc.*, 108, 3415 (1986).

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